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The Trans-Cis Isomerisation of Bis(dioxolene)bis(pyridine)Ruthenium Complexes.

By

Y.-H. Tse, P.R. Auburn and A.B.P. Lever*

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The Trans-Cis Isomerisation of Bis(dioxolene)bis(pyridine) Ruthenium Complexes.

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The Trans-Cis Isomerisation of Bis(dioxolene)bis(pyridine) Ruthenium Complexes.

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Abstract:

The isomerisation of trans to cis bis(3,5-di-t-butylbenzo semiquinonato)bis(R-Pyridine)ruthenium, $[Ru(R\text{-}Py)_2(DTBDiox)_2]$, is induced by warming with an excess of R-Pyridine, where R = 3-chloro, 4-methyl, 4-phenyl or 4-butyl. The rates of these reactions, for the species with R-Py = 3-chloropyridine, were monitored in o-dichlorobenzene by uv-visible spectroscopy, against varying 3-chloropyridine and varying trans-$[Ru(3\text{-}ClPy)_2(DTBDiox)_2]$ concentration. The data were found to obey first order kinetics; $-d[Ru(3\text{-}ClPy)_2(DTBDiox)_2]/dt = k_{obsd}[Ru(3\text{-}ClPy)_2(DTBDiox)_2]$ over a considerable range of pyridine concentration. A plot of $1/k_{obsd}$ vs. [3-chloropyridine] is linear with a positive intercept. A dissociative mechanism is proposed for the isomerisation reaction. The activation parameters were determined for the specific case of R-Py = 3-chloropyridine. Electronic and electrochemical features of these species are briefly discussed.

KEYWORDS: Ruthenium; Quinone; Isomerisation; Electrochemistry; Electronic Spectra; NMR

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Introduction:

The series of complexes $Ru(NN)_2(diox)$ (1-3) and $Ru(NN)(diox)_2$ (3-7) have been described, where NN may be 2,2'-bipyridine or two substituted pyridines, R-Py, and (diox) is a dioxolene ligand which may exist in the catechol, semiquinone or quinone oxidation states. These complexes form redox series whose electronic structures have been probed by a range of techniques including X-ray crystallography, NMR, ESR, magnetism and UV/Vis/FTIR, PES and resonance Raman (rR) spectroscopy. The bipyridine-bis(dioxolene) complexes are necessarily cis, while the R-Py analogues could be either cis or trans.

The previously described trans-$Ru(R\text{-}Py)_2(diox)_2$ series of complexes (5,7) are found to be isomerised to a cis configuration when warmed with an excess of pyridine. Here we describe studies of the isomerisation reaction and electrochemical and optical data characterising these new cis species.

Experimental Section:

Equipment. All absorbance measurements were performed on a Hitachi-Perkin Elmer microprocessor model 340 spectrometer equipped with an electrically heated cell compartment connected to a built-in thermostat for temperature measurement and control. Fourier transform infrared (FTIR) data were obtained using a Nicolet SX20 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained with a Bruker AM300FT NMR spectrometer using samples dissolved in $CDCl_3$.

Electrochemical data were obtained with a Pine Instruments RDE-3 potentiostat. Cyclic voltammetry was carried out, in dichloroethane (DCE), using platinum wires as working and counter electrodes, and a AgCl/Ag quasi-reference electrode with ferrocene (Fc) as an internal standard. The Fc/Fc^+ couple lies at +0.425 V vs. SCE (7).

Materials. Tetrabutylammonium perchlorate (TBAP, Kodak) was recrystallised from absolute ethanol and dried in vacuo at 50°C for 2 days. 1,2-Dichlorobenzene (DCB) (Aldrich, HPLC grade) and d_8 toluene were used as supplied. 1,2-Dichloroethane (DCE) was fractionally distilled from P_2O_5. 3-chloropyridine (Aldrich) and 4-methylpyridine

(Aldrich), were fractionally distilled under reduced pressure. Other substituted pyridines (Aldrich) were used as supplied without any further purification.

Syntheses. The species trans-$Ru(R\text{-}Py)_2(DTBDiox)_2$ were prepared by the methods given previously (5,7).

Cis-$Ru(R\text{-}Py)_2(DTBDiox)_2$: Trans-$Ru(R\text{-}Py)_2(DTBDiox)_2$ (36 mg, ca 5.0×10^{-2} mmol) was dissolved in toluene (10 mL). R-pyridine (R = 3-chloro, 4-methyl or 4-phenyl) (2.1 mmol) was added. The resulting mixture was refluxed under nitrogen for 12 h, filtered hot and then concentrated using rotary evaporation; methanol (1 mL) was then added to initiate crystallisation. The products were filtered, washed with cold methanol and air dried; yield ~80%. Anal: Found C 59.48; H 6.27; N 3.64. Calc. C 59.37; H 6.29; N 3.64. for R = 3-chloro; Found C 64.70; H 7.44; N 3.88. Calc. C 64.40; H 7.60; N 3.76. for R = 4-methyl, monohydrate; Found C, 68.70, H. 6.86, N, 3.53. Calc. C, 69.0, H, 6.95, N, 3.21 for R = 4-Phenyl, monohydrate. The trans species used for the kinetic measurements had acceptable C, H, N analyses (7).

^1H NMR data for R = 3-chloropyridine species, in $CDCl_3$. Data for the trans isomer from (7). (s = singlet, d = doublet, dd = doublet-doublet, m = multiplet) - trans-isomer 7.74 (d, J = 2.2 Hz, 2H); 7.63 (d, J = 2.0 Hz, 2H); 7.6 (dd, J = 5.4, 1.1 Hz, 2H); 7.23 (m, 2H); 6.87 (dd, J = 8.2, 5.7 Hz, 2H); 6.17 (br s, 2H); 1.62 (s, 18H); 1.35 (s, 18H). cis-isomers 8.54 (m); 8.27 (m); 8.04 (d, J = 2.2 Hz); 7.73 (m); 7.57 (m); 7.14 (m); 6.90 (m); 6.80 (m); 6.70 (d, J = 2.1 Hz); 1.77 (s); 1.67 (s); 1.37 (s); 1.36 (s); 1.33 (s); 1.20 (s); 0.89 (s); 0.88 (s).

Kinetic Studies. DCB was used as the solvent for the rate studies unless otherwise stated. The liquid 3-chloropyridine (8.40×10^{-5} mole to 1.05×10^{-3} mole) was mixed with 4 mL of a stock solution of trans-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$ and diluted to 5 mL [(trans-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$ = (2.07×10^{-4} M)]. The reaction mixture was transferred to a 1 cm cell which was placed into a pre-heated cell compartment; the temperature of the solution inside the cell was measured before and after each experiment (variation ± 0.25°C). Successive spectra were collected at time intervals from 2.8 min to 100 min, depending upon

the temperature and concentration range involved.

The isomerisation from trans --> cis-Ru(3-ClPy)$_2$(DTBDiox)$_2$ was monitored by observing the growth of a new absorption band lying close to 600 nm (6) observed for the cis isomer. The trans isomer possesses very weak absorption at this wavelength (Figure 1).

For the pseudo-first-order conditions, the observed rate constants (k_{obsd}) were obtained from the Guggenheim plots (8). The reactions were allowed to proceed for 3 - 4 half-lives. The delay time was about 2 half-lives.

Rate constants for isomerisation of trans-Ru(3-ClPy)$_2$(DTBDiox)$_2$ (2.07×10^{-4} M), in DCB, at various temperatures from 91 to 110°C are presented here as a function of the concentration of 3-chloropyridine. Values of [3-chloropyridine] are tabulated, together with k_{obsd}, (all values to be multiplied by 10^{-4} s^{-1}), followed by the standard deviation in parentheses.

Temp. °C [3ClPy]	0.016	0.03	0.06	0.08	0.1	0.2 M
91	1.64	1.24	0.89	0.857	0.787	0.496
	(0.01)	(0.02)	(0.01)	(0.002)	(0.001)	(0.001)
96	3.19	2.67	2.14	1.87	1.64	1.06
	(0.03)	(0.02)	(0.02)	(0.01)	(0.01)	(0.01)
100	5.97	5.33	3.99	3.71	3.50	2.24
	(0.04)	(0.06)	(0.01)	(0.04)	(0.03)	(0.01)
105	11.4	9.7	7.4	6.41	6.16	4.26
	(0.21)	(0.19)	(0.1)	(0.06)	(0.06)	(0.04)
110	18.89	18.1	14.61	13.3	12.1	9.02
	(0.73)	(0.5)	(0.07)	(0.15)	(0.2)	(0.07)

Data were also obtained, at 90° C, for constant [3-chloropyridine] = 0.16 M, and varying trans-Ru(3-ClPy)$_2$(DTBDiox)$_2$ over the range from about 1×10^{-4} to 5.4×10^{-4} M, with no significant variation in k_{obsd}.

The isomerisation of $Ru(3\text{-}ClPy)_2(DTBDiox)_2$ in d_8-toluene at 93°C was followed by ^1H NMR ([$Ru(3\text{-}ClPy)_2(DTBDiox)_2$] = 2.72×10^{-3} M; [3-chloropyridine] = 0.5 M).

Results and Discussion:

The trans-$Ru(R\text{-}Py)_2(DTBDiox)_2$ species are best regarded as fully delocalised trans-Ru(III)$(R\text{-}Py)_2$(DTBCat(-2))(DTBSq(-1)) species (so-called (S) (starting) species in previous discussions) (3-5,7). Their electronic spectra are typified by a very intense absorption near 1100 nm attributed to diox (π) --> Ru($d\pi$) + diox (π^*) IL + LMCT (Fig.1). They display only weak absorption in the visible region (near 580 nm (7)).

Synthesis of the cis complexes, and background literature:

When a trans-$Ru(R\text{-}Py)_2(DTBDiox)_2$ complex is warmed with a pyridine, a band near 600 nm (Table 1), grows in at a rate which depends upon temperature, concentration of pyridine, and nature of the R substituent (Fig.2). Isomerisation proceeds within a fairly narrow range of pyridine concentrations. If a large excess of pyridine (> 10^4 [$Ru(R\text{-}Py)_2(DTBDiox)_2$]) is used, a side reaction takes place, probably forming the tetrapyridine species, and the isosbestic point is lost. The trans isomer undergoes another side reaction if insufficient pyridine (< 10 [$Ru(R\text{-}Py)_2(DTBDiox)_2$]) is used. Heating either the cis or trans isomer in an inert solvent, in the absence of an excess of pyridine ligand, led to eventual decomposition. Isomerisation occurs cleanly when the pyridine to ruthenium ratio lay approximately in the range 10^2 - 10^3.

The final electronic spectrum has the same overall band envelope as that (6) of cis-Ru(bpy)$(DTBDiox)_2$ (save for the absence of the Ru ---> bpy CT transition), providing evidence that isomerisation has occurred. The absorption near 600 nm (Table 1) corresponds with a n--> π^* semiquinone transition allowed in the cis isomer but forbidden in the trans isomer (5,7). Further, cis complexes were isolated (see expt.) and their NMR spectra (Expt.) leave no doubt that cis-$Ru(R\text{-}Py)_2(DTBDiox)_2$ species have been formed. Under the experimental conditions used to prepare the trans isomer, no cis isomer is isolated (7).

A number of cis-trans isomerisations of ruthenium complexes have been previously reported. It is revealing to contrast their behaviour. The species cis-$[Ru(bpy)_2(H_2O)_2]^{2+}$ is photo-isomerised to the trans species by a dissociative pathway (9), but no thermal route was reported. The species trans-$Ru(dppm)_2Cl_2$ (dppm = bis-diphenylphosphinomethane) can readily be thermally isomerised to the cis isomer in halocarbon solvents (at 83° C (reflux) in DCE) (10). This may be reversed (cis --> trans) photochemically (10). Oxidation of cis-$Ru^{II}(dppm)_2Cl_2$ leads to isomerisation to the trans-Ru^{III} species, and the formation of trans-$Ru(dppm)_2Cl_2$ upon subsequent reduction (10). The complex cation trans-$[Ru(acac)_2(CH_3CN)_2]^{2+}$ is thermally isomerised to the cis species, at 30° C with a half-life of about 9 days (11). Data for cis and trans-$[RuCl(NO)(bpy)_2]^{2+}$ have been reported (12), but no inter-conversion experiments were reported. Some bis(dithiocarbamate)nitrosyl complexes of ruthenium, such as cis-$Ru(NO)(S_2CNMe_2)SCN$ can be thermally converted to the corresponding trans isomer, in the solid state, at 220°C (13). Transformations in the rather more complex $Ru(AzPy)_2Cl_2$ (AzPy = 2-phenylazopyridine) have also been explored (14). A very detailed contribution discusses the formation of all trans, ttt-$Ru(CO)_2Cl_2(PR_3)_2$ species which isomerise in chloroform at from 50°C (actual temperature depending upon the phosphine) to the all cis, ccc-$Ru(CO)_2Cl_2(PR_3)_2$ species which then isomerises to the thermodynamically stable cct-$Ru(CO)_2Cl_2(PR_3)_2$ species (15). Our systems appear to be the first ruthenium species to be reported where isomers may be isolated by addition of an external common ligand (vide infra).

Nuclear Magnetic Resonance Studies: Trans-$Ru(R\text{-}Py)_2(DTBDiox)_2$ complexes can exist in two forms with C_{2h} and C_{2v} symmetry depending upon the relative orientation of the t-butyl groups. Previously we have demonstrated (7) that for all of these complexes, only two t-butyl resonances are observed for the DTBDiox ligands indicative of a single isomer having been prepared. The X-ray data (3) for both the (S) trans-$Ru(4\text{-}t\text{-}BuPy)_2(DTBDiox)_2$ and the oxidised (O1) trans-$[Ru(3\text{-}ClPy)_2(DTBDiox)_2]^{+}$ cation show that these trans isomers in the

solid state have C_{2h} symmetry.

The cis-Ru(R-Py)$_2$(DTBDiox)$_2$ species can exist as three different geometric isomers which could give rise to eight t-butyl resonances in their ^{1}H NMR spectra (Exot.). Four different t-butyl resonances arise from two cis isomers with same C_2 symmetry (so-called symmetric isomers). Another four different t-butyl resonances come from the third cis isomer which has C_1 symmetry (asymmetric isomer). In fact, these eight t-butyl resonances are observed for cis-Ru(3-ClPy)$_2$(DTBDiox)$_2$, although we have been unable to separate these three cis isomers.

When isomerisation of the trans-Ru(3-ClPy)$_2$(DTBDiox)$_2$ species was followed by NMR, in d_8-toluene, the resonances for all three cis isomers grew in at approximately the same rate (16).

Electrochemistry: The electrochemical behaviour of the cis-Ru(R-Py)$_2$(DTBDiox)$_2$ species is very similar to that of the trans analogues (Table 3). Assignments have been discussed in depth previously (6,7). Arguments have been expressed in the literature relating differences in the electrochemical behaviour of cis and trans pairs, to differences in electronic structure. Thus the ruthenium centred waves observed with the cis and trans [RuCl(NO)(bpy)$_2$]$^{2+}$ nitrosyl species (12) differ by only 10 mV, but there is a substantial difference (170 mV) in the nitrosyl reduction wave for these two isomers, implying some marked structurally dependent electronic changes localised on the nitrosyl group. The M^{III}/M^{II} potentials for the pairs of cis and trans isomers M(dppm)$_2$Cl$_2$ (M = Os, Ru) (10), differ by 370 mV (Ru) and 460 mV (Os) with the cis isomers being the most difficult to oxidise, the difference being attributed to the difference in π-back-bonding capability in the pairs of isomers. Where more than one π-accepting ligand is present, such as in the series [Ru(dppm)$_2$(CO)X]$^+$ and [Ru(bpy)(dppe)(CO)X]$^+$ (X = Cl, Br, I) (17), the trans isomer is more difficult to oxidise by up to 450 mV. In our dioxolene system, couple V (Table 3) is most closely associated with the Ru^{III}/Ru^{II} couple (6,7). The lack of any shift in this couple between cis and trans isomer arises because at this oxidation level, the Ru^{II} is bound to the

non-π-accepting catechol. The remaining couples involve redox processes which are more localised on the dioxolene residues and are, accordingly, less sensitive to the geometry of the isomer.

Kinetic Studies:. The kinetics of the isomerisation reactions of $Ru(3\text{-}ClPy)_2(DTBDiox)_2$ (2.07×10^{-4} M) were investigated at various temperatures with 3-chloropyridine concentrations ranging between 1.6×10^{-2} M and 2×10^{-1} M (see Expt.) Values of k_{obsd} were derived from a Guggenheim plot (8) (Figure 3). The reaction followed pseudo-first-order kinetics:

[1] $$-d[Ru(3\text{-}ClPy)_2(DTBDiox)_2]/dt = k_{obsd}[Ru(3\text{-}ClPy)_2(DTBDiox)_2]$$

over at least for four half-lives. Values of k_{obsd} at constant [3-chloropyridine] were independent of the concentration of $[Ru(3\text{-}ClPy)_2(DTBDiox)_2]$.

Plots of $1/k_{obsd}$ against [3-chloropyridine] were linear (Figure 4). This linearity is consistent with the following mechanism:

[2] $$\underline{trans}\text{-}Ru(3\text{-}ClPy)_2(DTBDiox)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(3\text{-}ClPy)(DTBDiox)_2 + 3\text{-}ClPy$$

[3] $$Ru(3\text{-}ClPy)(DTBDiox)_2 \xrightarrow{k_r} [Ru(3\text{-}ClPy)(DTBDiox)_2]^*$$

[4] $$[Ru(3\text{-}ClPy)(DTBDiox)_2]^* + 3\text{-}ClPy \rightleftharpoons \underline{cis}\text{-}Ru(3\text{-}ClPy)_2(DTBDiox)_2$$

Assuming step [4] is fast and using the steady-state approximation (8) for $[Ru(3\text{-}ClPy)(DTBDiox)_2]$, the rate of isomerisation is:

[5] $$-d[\underline{trans}\text{-}Ru(3\text{-}ClPy)_2(DTBDiox)_2]/dt$$
$$= \{(k_1k_r)/(k_{-1}[3\text{-chloropyridine}] + k_r)\}[\underline{trans}\text{-}Ru(3\text{-}ClPy)_2(DTBDiox)_2]$$
$$= k_{obsd}[\underline{trans}\text{-}Ru(3\text{-}ClPy)_2(DTBDiox)_2]$$

The calculated k_1 and k_{-1}/k_r derived respectively from the intercept ($1/k_1$) and the slope (k_{-1}/k_1k_r) are listed in Table 2. An Arrhenius plot of $\ln(k_1)$ versus inverse temperature led to an activation energy of 148 ± 6 kJ/Mole, and, using the Eyring expression

(8), an activation entropy of 88 ± 17 J/Mole.

The data (Figure 4) are consistent with a dissociative mechanism in which a pyridine ligand is lost to form a five coordinate intermediate which can either re-attach the pyridine ligand and return to the trans isomer, or undergo a twist, first to form two different trigonal bipyramidal intermediates (e.g. see (15)) differing in the orientation of the t-butyl groups on the dioxolene ligands. These two intermediates can be interchanged by a pseudo-rotation. When the pyridine ligand is re-attached to these intermediates, all three cis isomers are formed. Ligand loss and formation of the five coordinate intermediate lead to alternative decomposition pathways when insufficient pyridine is present to trap the intermediate.

The positive activation entropy value associated with reaction [1] is consistent with the dissociative mechanism (15,18-21). Indeed both the activation enthalpy and entropy have values close to those reported previously for mechanisms involving the loss of a ligand from a six coordinate ruthenium(II) species (15,20). Specifically there is a close similarity between the activation data reported here and those detailed for the isomerisation of the $Ru(CO)_2Cl_2(PR_3)_2$ species (15).

A mixed ligand experiment shows that the rate of isomerisation of trans-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$ in the presence of bulk 4-methylpyridine is different from that with bulk 3-chloropyridine (and vice versa). Although additional kinetic data cannot readily be extracted because the electronic spectra of the various R-Py species do not differ sufficiently, the result supports the proposed mechanism.

Electronic spectra:

The electronic spectra of these new cis species reveal some subtle but important differences from the previously reported (7) spectra of the trans species. The NIR band in the cis-S species shifts slightly to lower energy with more electron donating pyridine ligands (Table 1), consistent with the MLCT Ru d --- > semiquinone (π^*) transition, previously assigned in the spectra of the analogous bipyridine species (6). The lower energy of this band

in the pyridine series, relative to the bipyridine series, arises from the greater stabilisation of the d orbitals by the bipyridine ligand. There is no shift with pyridine substituent in the spectra of the trans-S species (7), for the corresponding band which has little CT character.

The behaviour of the second band, near 600 nm, is more ambiguous, but does shift to the red with the more electron accepting 3-chloro substituent. This is an n ---> π^* transition which evidently has some LMCT character.

The third band, near 400 nm, is evidently Ru ($d\pi$) ---> R-Py (π^*), since it shifts to lower energy in the sequence 4-methyl > 3-chloro > 4-Phenyl, this last having an especially low energy π^* orbital extending over the phenyl group.

To confirm certain subtle conclusions concerning the differences in electronic structure between the cis and trans series, some of these species were oxidised, with silver ion, to the O1 species, to obtain their electronic spectra. These O1 complexes, which were not isolated,have spectra closely related to the spectra of the cis-O1 bipyridine analogues (6) rather than to their trans-O1 relatives. Thus the main band has MLCT Ru ($d\pi$) ---> semiquinone (π^*) character and shifts to lower energy with the more electron donating pyridines. The corresponding band in the trans species (transition O1,II), (7) has LMCT character and shifts in the opposite sense with pyridine substituent. The shifts in the second band, near 520 nm, are too small to comment upon.

These data support previous assignments, (6,7) and indeed add useful corroboratory evidence. The contrasting dependencies upon dioxolene and pyridine substituents, arise from changes in the degree of mixing of metal and ligand orbitals due to the symmetry restrictions imposed by the two geometries (7). The cis isomers are concluded to parallel the bipyridine species in having somewhat more Ru^{II} character than their trans analogues (7).

Conclusion:

Trans-Ru(R-Py)$_2$(DTBDiox)$_2$ (C_{2h}) species are kinetically favoured products during synthesis and are isomerised to their corresponding cis isomers by warming with an excess of a pyridine. A dissociative mechanism for this trans --> cis isomerisation is proposed.

The electrochemical and optical data for the trans and cis isomers of $Ru(R\text{-}Py)_2(DTBDiox)_2$ are compared. The electronic spectra support previous assignments given for the corresponding cis-bpy complexes (6). Detailed analysis further corroborates earlier arguments (5-7, 22) concerning the degree of mixing between metal and ligand orbitals, and the formal oxidation states of these species.

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16. This, in fact, differs from the behaviour of the corresponding bipyridine complexes, in which only two of the three possible isomers are obtained. Previously (6), we reported that all three isomers were present. This was in error - the seven peaks in the t-butyl

region of the ^1H NMR spectra being due to two isomers (C_1 and C_2 symmetry) and to water. The presence of only two isomers was clearly confirmed by TLC.

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Table 1

Electronic Spectroscopic Data for cis-Ru(R-Py)$_2$(DTBDiox)$_2$, (S), and cis-[Ru(R-Py)$_2$(DTBDiox)$_2$]$^+$, (O1), complexes[a,b]

Complex	λ_{max}/nm		
cis-Ru(3-ClPy)$_2$(DTBDiox)$_2$	1001	595	394
cis-Ru(4-MePy)$_2$(DTBDiox)$_2$	1028	587	362(sh)
cis-Ru(4-PhPy)$_2$(DTBDiox)$_2$	1009	597	412
cis-Ru(4-BuPy)$_2$(DTBDiox)$_2$	1017	590	366
cis-Ru(3-ClPy)$_2$(DTBDiox)$_2^+$	738	519	379(sh) 305(sh)
cis-Ru(4-MePy)$_2$(DTBDiox)$_2^+$	748	511	378(sh) 315(sh)
cis-Ru(4-PhPy)$_2$(DTBDiox)$_2^+$	743	526(sh)	369(sh)
cis-Ru(4-BuPy)$_2$(DTBDiox)$_2^+$	761	513	371(sh)

a) solvent: DCE Data for the cis (S) species from solid starting materials. b) Oxidised (O1) species are prepared by the oxidation of S species with Ag^+ ions in DCE, followed by filtration through Celite.

Table 2 Rate Constants k_1 and k_{-1}/k_r for Isomerisation of trans-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$ at Different Temperatures.[a]

Temp. K	k_1 (x 10^{-4} s)	k_{-1}/k_r (M)
91	1.74(0.19)	12.7(2.2)
96	3.76(0.08)	12.7(0.4)
100	6.82(0.41)	10.2(1.0)
105	12.0(0.1)	9.4(1.5)
110	20.7(0.1)	6.7(0.5)

a) Data derived from the k_{obsd} data cited in Experimental section.

Standard deviation in parenthesis.

Table 3

Electrochemical Data for $Ru(NN)_2(DTBDiox)_2$ Complexes[a]

Complex	$E_{1/2}$ (V) vs. SCE			
	II	III	IV	V
trans-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$[b]	+1.08	+0.30	-0.60	-1.51qr
cis-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$	+1.01	+0.35	-0.71	-1.54qr
cis-Ru(bpy)$(DTBDiox)_2$[c]	+1.00	+0.31	-0.71	-1.42

a) Measurements were made using 1,2-dichloroethane solutions of the starting materials (10^{-3}M) containing 0.2M TBAP. $E_{1/2}$ values are obtained from the cyclic voltammetry at 100mVs^{-1}. qr = quasi-reversible. For assignment of the redox couples, see refs.(6.7). b) ref.(7). c) ref.(6). The assumed position of the Fc^+/Fc couple used in reference (6) differed by +0.115 V relative to that assumed here. The potentials taken from reference (6) have been appropriately corrected.

Figure Legends

Figure 1. Visible-Near infrared spectra for cis-(.) and trans-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$ (-) in 1,2-dichloroethane.

Figure 2.

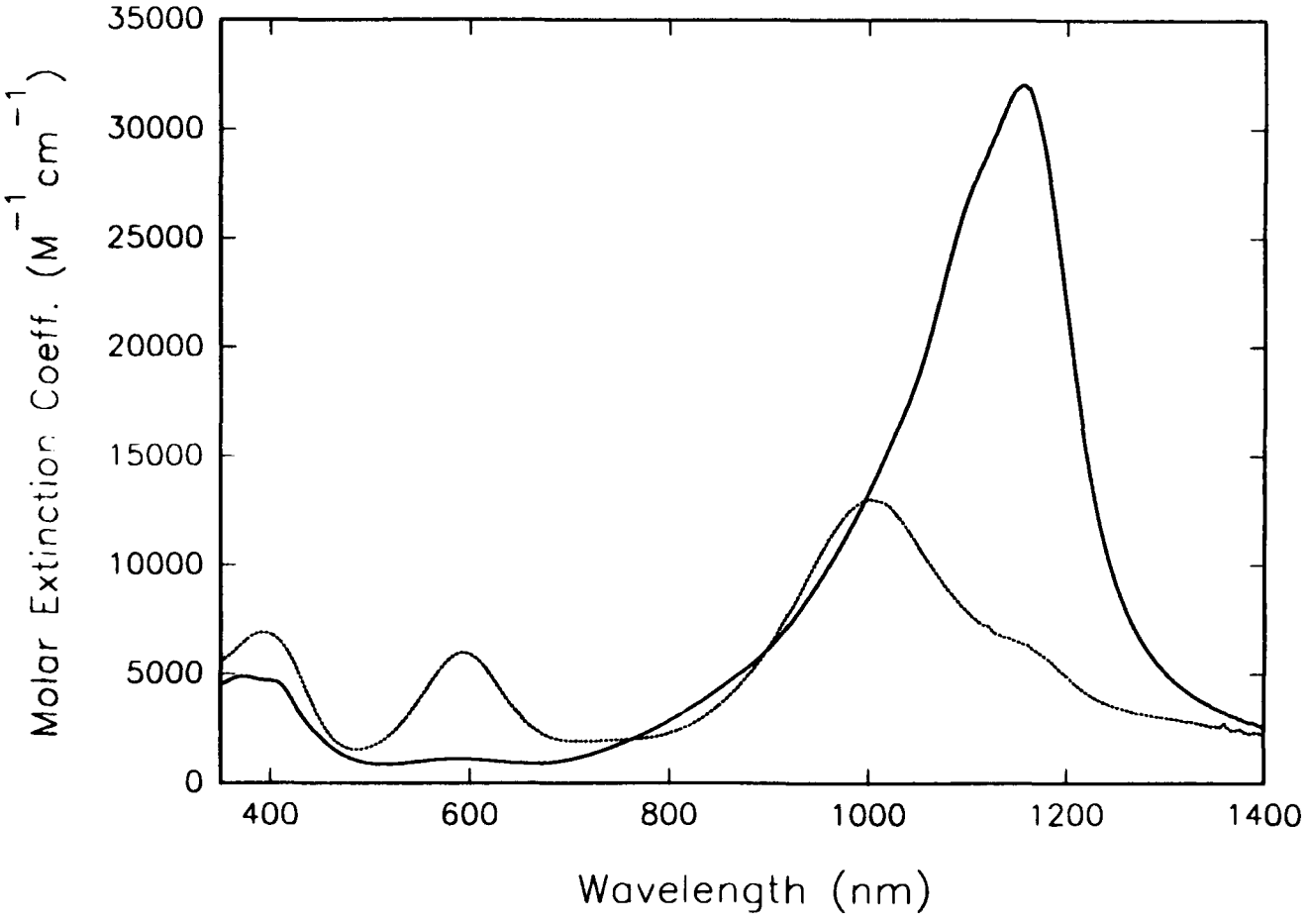
A typical data set showing successive scans of the visible spectrum during the isomerisation of trans-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$ (2.07×10^{-4}M) in the presence of an excess of 3-chloropyridine (1.0×10^{-1} M) at 100°C in o-dichlorobenzene. The first scan in the experiment was not recorded on the spectrum.

Figure 3.

Guggenheim Plot using data from Figure 2 at wavelength = 600 nm for the isomerisation of the trans-$Ru(3\text{-}ClPy)_2(DTBDiox)_2$ complex. The delay time in the Guggenheim plots is approximately two half-lives.

Figure 4.

Plots of $1/k_{obsd}$ vs. [3-chloropyridine] for the isomerisation of $Ru(3\text{-}ClPy)_2(DTBDiox)_2$ at 100°C, in o-dichlorobenzene, at (from upper to lower), 91, 96, 100, 105 and 110 °C.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30000
25000
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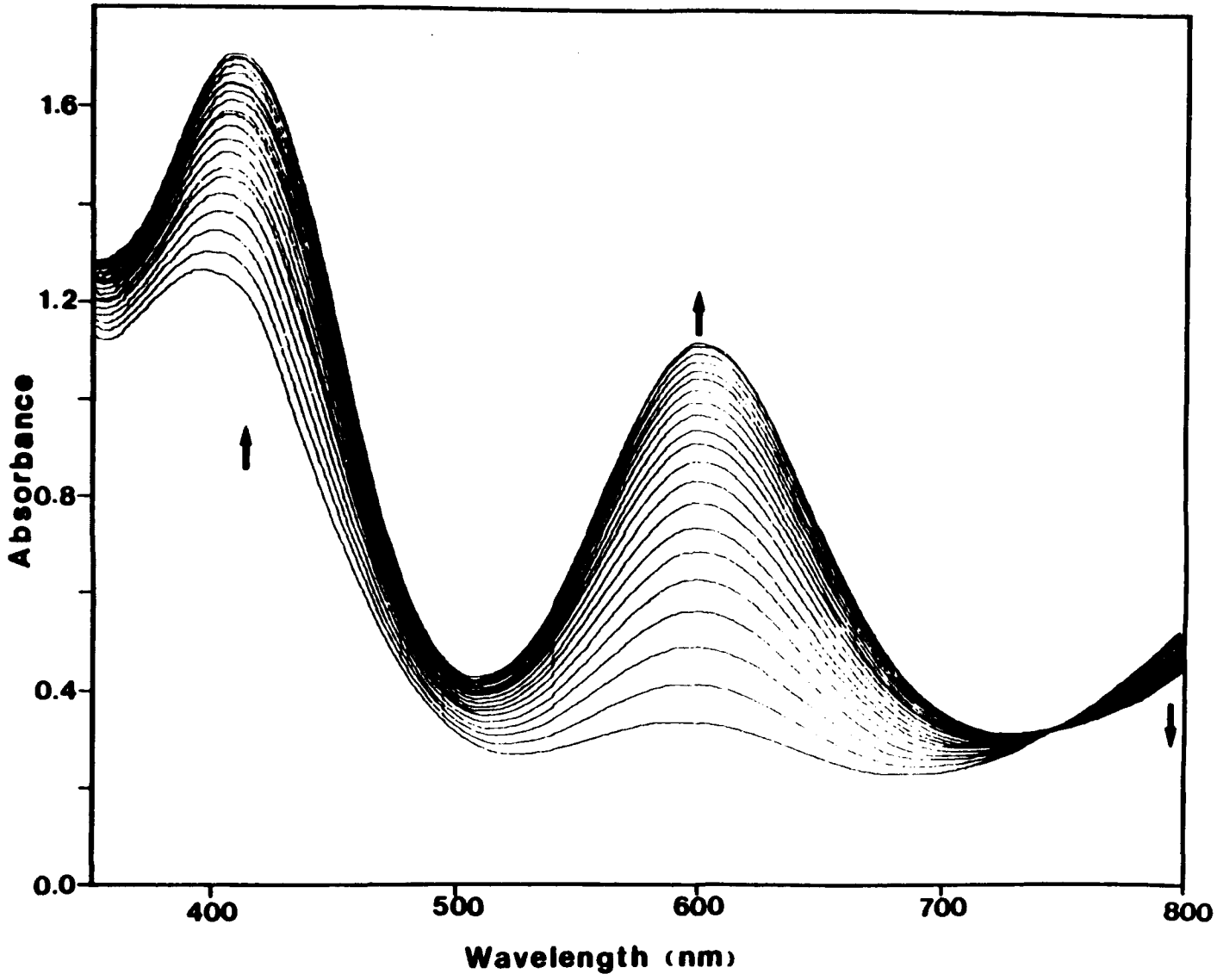
600
800
1000
1200
1400
Wavelength (nm)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1.2
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0.4
0.0
Absorbance
400
500
600
700
800
Wavelength (nm)

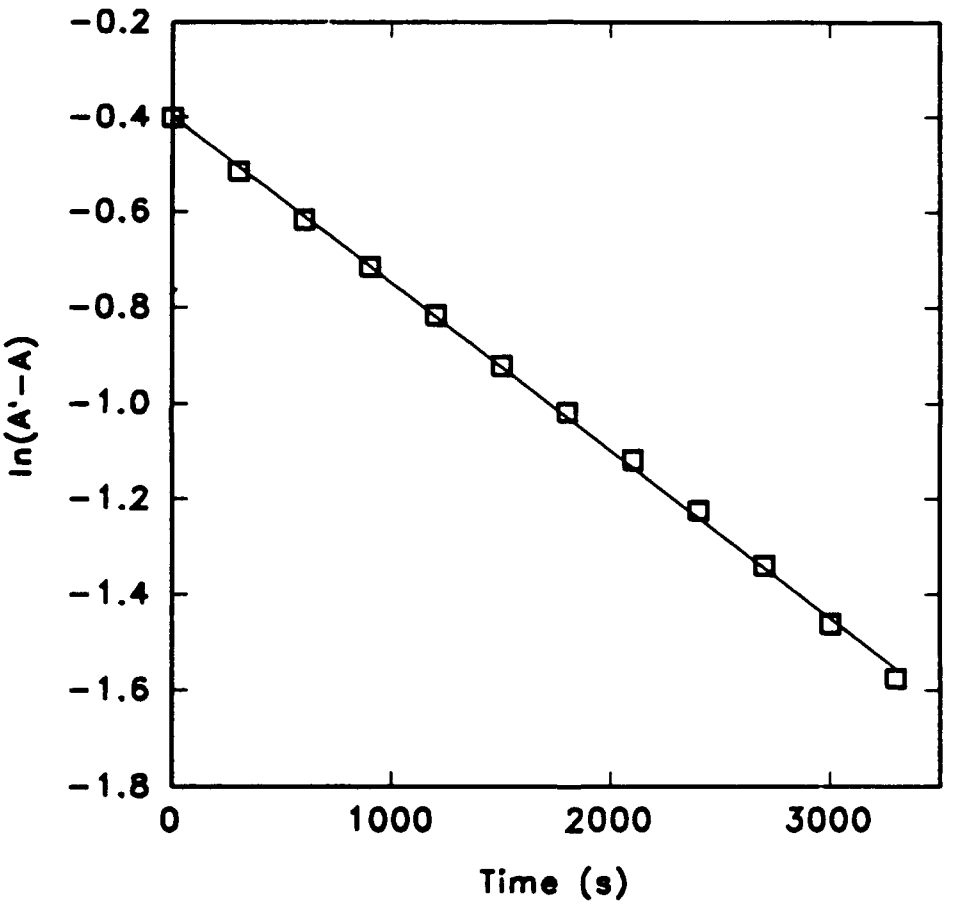
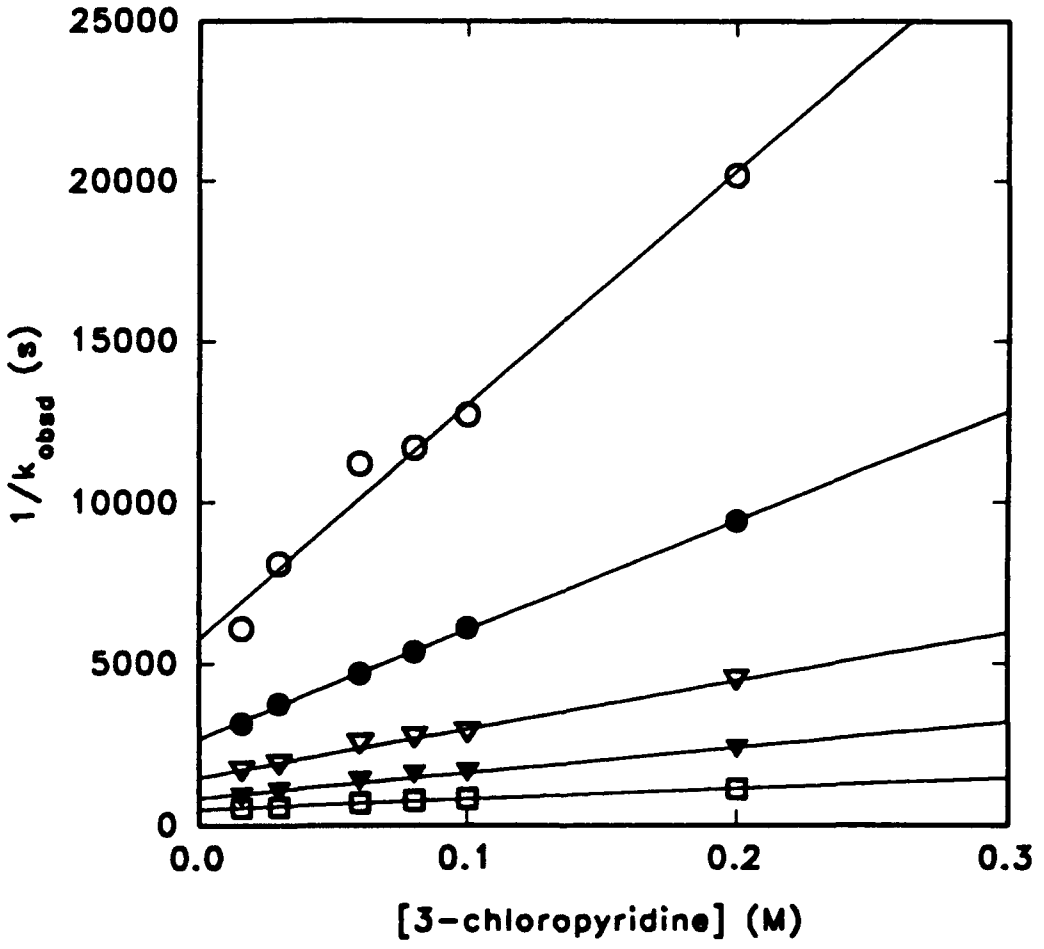


Fig 3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20000
15000
10000
5000
0
1/k obsd (s)
0.0
0.1
0.2
0.3
[3-chloropyridine] (M)

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